Enhancement of the photocatalytic reactivity of TiO$_2$ nano-particles by a simple mechanical blending with hydrophobic mordenite (MOR) zeolite

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ABSTRACT

The photocatalytic oxidation of gaseous acetaldehyde with O$_2$ on commercial TiO$_2$ nano-particles could be successfully enhanced by a simple mechanical blending with a high-silica mordenite (MOR) zeolite, the surface of which showed high hydrophobic properties. When the TiO$_2$ nano-particles of ca. 5–20 wt% were mixed with the MOR zeolite powders in an agate mortar for only 5 min, the blended TiO$_2$/MOR samples showed higher photocatalytic reactivity as compared to the pure TiO$_2$ nano-particles. Since the high-silica zeolite powders are highly transparent in UV light regions, the incident UV light is effectively irradiated onto the whole part of the TiO$_2$ nano-particles without any loss of light intensity. Furthermore, the siliceous MOR zeolite powders effectively adsorb the gaseous acetaldehyde molecules and supply them onto the surfaces of the blended TiO$_2$ nano-particles, resulting in an enhancement of the photocatalytic reactivity.

1. Introduction

Since TiO$_2$ photocatalysts originally have the potential to completely decompose harmful organic compounds into CO$_2$ and H$_2$O under UV light irradiation, they have been widely studied for the purification of air, water, and soil polluted with organic compounds [1–4]. Various air-cleaning and deodorization systems equipped with TiO$_2$ photocatalysts and UV light sources that reduce volatile organic compounds (VOCs), such as aldehydes, carboxylic acids, and aromatic compounds which can cause the so-called "sick house syndrome" are now commercially available. However, the removal efficiencies of air-cleaning systems for odorant compounds in the home environment still needs to be improved by as simple and low-cost method as possible. Although the deposition of small amounts of Pt on TiO$_2$ catalyst surfaces is generally known to enhance the photocatalytic reactivity [5–9], Pt is expensive and Pt compounds are too costly for common use in home electrical appliances. On the other hand, the hybridization of adsorbents such as zeolites, mesoporous materials [10–15] or activated carbon [16–18] with TiO$_2$ particles has been reported to show elevated photocatalytic reactivity, especially for the decomposition of gaseous organic compounds. In our previous report [19], the hybridized TiO$_2$/ZSM-5 catalysts prepared by a simple impregnation method also showed high photocatalytic reactivity for the complete oxidation of gaseous acetaldehyde as compared to the pure TiO$_2$ catalyst since the ZSM-5 zeolite powders are able to efficiently adsorb acetaldehyde molecules diffused in wide spaces and then smoothly supply them onto the TiO$_2$ photocatalyst surfaces.

In this work, TiO$_2$ nano-particles were mechanically blended with the hydrophobic MOR zeolite in a simple preparation method in order to maximize the photocatalytic performance of the commercial TiO$_2$ powders as well as reduce the preparation cost. The photocatalytic reactivity of the blended TiO$_2$/MOR systems was then evaluated for the complete oxidation of gaseous acetaldehyde with O$_2$ under UV light irradiation.

2. Experimental

TiO$_2$ nano-powdered photocatalysts (SSP-25, anatase phase, SSA$_{BET}$ = ca. 270 m^2/g) and the highly siliceous H$^+$-type MOR zeolite (HSZ-690-HOA, SiO$_2$/Al$_2$O$_3$ = 240, SSA$_{BET}$ = ca. 460 m^2/g) were purchased from Sakai Chemical Industry Co., Ltd. and Tosoh Co., Ltd., respectively. TiO$_2$/MOR photocatalysts having different TiO$_2$ content were obtained by a simple mechanical blending of these two powder samples in an agate mortar for 0–60 min

[described as TiO$_2$/MOR(A)]. For comparison, a different type of TiO$_2$/MOR photocatalysts was also prepared by an ultrasonic aqueous suspension of these two powder samples [described as TiO$_2$/MOR(B)]. The TiO$_2$ nano-powders blended with the MOR zeolites were then characterized by XRD (Shimadzu, XRD-6100) and diffuse reflectance UV–vis absorption (Shimadzu, UV-2200A) measurements at room temperature.

The photocatalytic reactivities of the blended TiO$_2$/MOR samples were evaluated for the decomposition of gaseous acetaldehyde in the presence of O$_2$ under UV light irradiation. The TiO$_2$/MOR catalysts (50 mg) were placed onto a flat bottom quartz cell (volume, ca. 33 cm^3). The volume of the reaction area including the cell volume was ca. 100 cm^3. Before photoreactions, the catalysts were degassed at 723 K for 2 h, treated in sufficient amounts of O$_2$ (ca. 6.7 kPa) at the same temperature for 2 h, and then degassed at 373 K for 2 h up to a 10^{-5} kPa range. A gas mixture of CH$_3$CHO (0.27 kPa), O$_2$ (1.07 kPa), and H$_2$O (0–1.33 kPa) was then introduced into the reaction cell. The amount of acetaldehyde introduced into the reaction cell was calculated as ca. 8 μmol (ca. 1500 ppm). After an adsorption equilibrium was reached, UV light was irradiated at 275 K by a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (Toshiba Glass, UV-27, λ > 270 nm, ca. 1–2 mW/cm^2). To avoid the heating effect from the UV lamp, the photocatalysts in the quartz cell were cooled in ice water during the photoreactions. The amount of CO$_2$ produced and acetaldehyde decomposed were analyzed by TCD (thermal conductivity detector) and FID (flame ionization detector) by gas chromatography (Shimadzu, GC-14A).

3. Results and discussion

Fig. 1 shows the XRD patterns of the TiO$_2$ nano-powders blended with MOR zeolites of different TiO$_2$ content. The TiO$_2$ nano-powder showed typical diffraction patterns attributed to the (1 0 1) phase of an anatase structure at around 26°. The primary particle size of the TiO$_2$ nano-powder (SSP-25) could be estimated at ca. 8 nm by Scherre's equation. On the other hand, all diffraction patterns for the zeolite which could be assigned to a MOR structure much sharper than the TiO$_2$ nano-powder, showing the largely grown zeolite
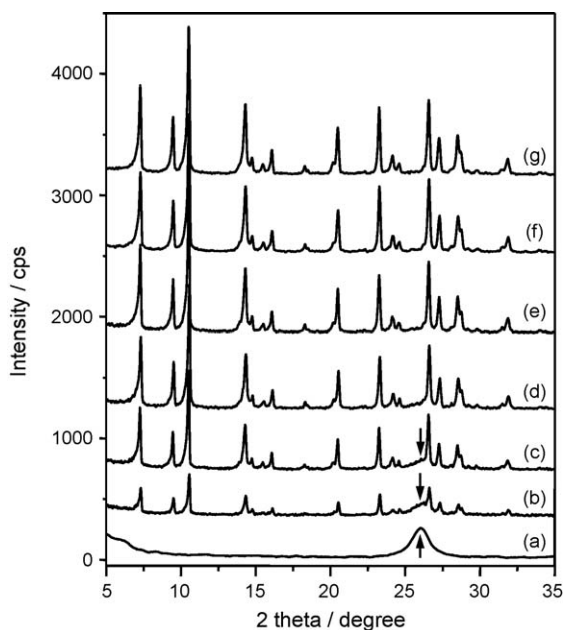
Fig. 1. XRD patterns of the TiO$_2$ nano-particles mechanically blended with the MOR (SiO$_2$/Al$_2$O$_3$ = 240) zeolite powders. TiO$_2$ contents (wt%): (a) 100, (b) 50, (c) 20, (d) 10, (e) 5, (f) 1, (g) 0.
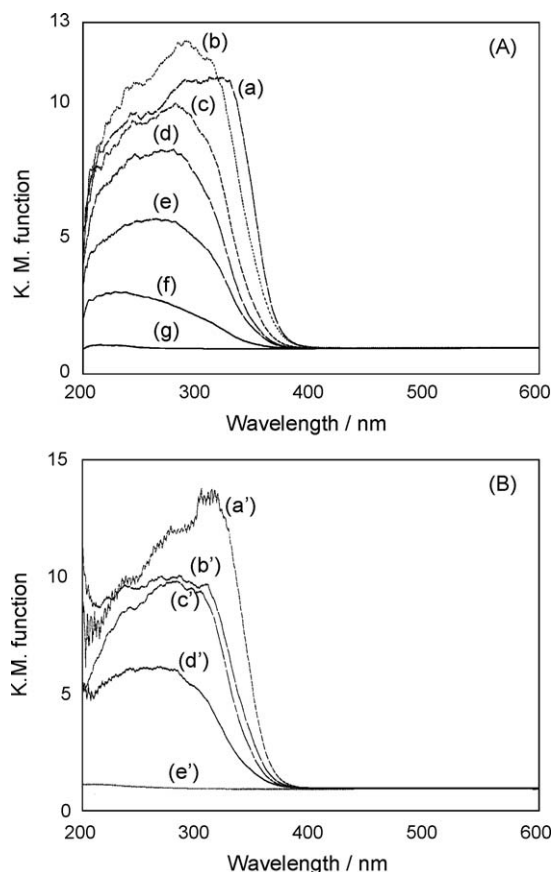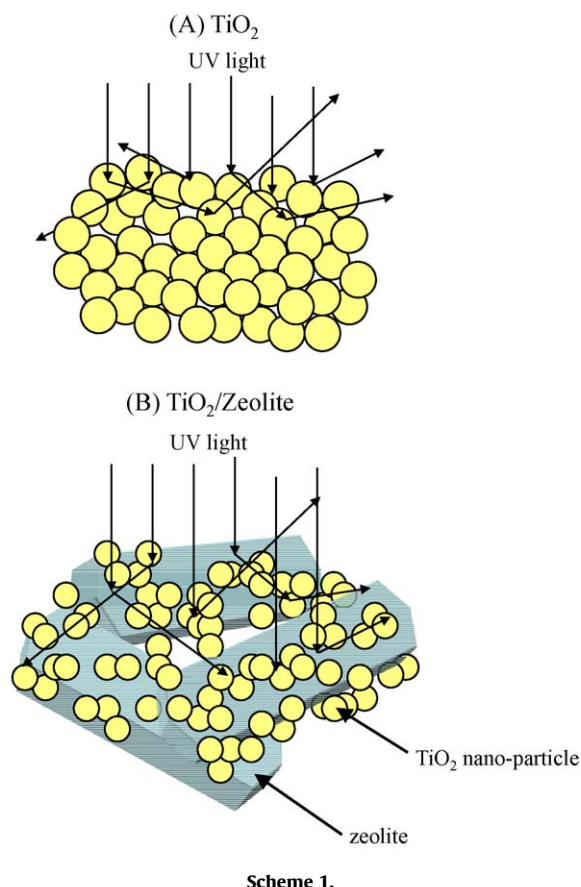
Fig. 2. Diffuse reflectance UV–vis absorption spectra of the TiO$_2$ nano-particles mechanically blended with (A) MOR zeolite and (B) non-porous SiO$_2$ powders. TiO$_2$ contents (wt%): (a, a′) 100, (b, b′) 50, (c, c′) 20, (d) 10, (e, d′) 5, (f) 1, (g, e′) 0.

crystals. When small amounts of TiO$_2$ nano-powders were mechanically blended with such largely grown zeolite particles for only 5 min, it became difficult to observe the diffraction patters due to the TiO$_2$ nano-powders. However, as the TiO$_2$ content increased up to 20 wt%, a broad diffraction peak attributed to the anatase (1 0 1) phase could be observed at around 26°.

The diffuse reflectance UV–vis absorption spectra of the TiO$_2$ nano-particles mechanically blended with siliceous MOR zeolite and non-porous pure SiO$_2$ powder are shown in Fig. 2A and B, respectively. The absorption edges of the TiO$_2$ nano-powders blended with the MOR zeolites were observed at around 380–400 nm. When smaller amounts of TiO$_2$ powders than 5 wt% were blended with the siliceous MOR or SiO$_2$ powders, some portion of the incident light was found to pass through the powder samples of several millimeters thickness due to the high transparency of the MOR and SiO$_2$ powders. When the amount of TiO$_2$ nano-powders blended with the zeolite powders reached about 10–20 wt%, the incident light could not penetrate the mixed powder samples, suggesting efficient irradiation of UV light onto the entire TiO$_2$ nano-particles as shown in Scheme 1. However, since the absorption coefficient and of the TiO$_2$ powder in UV light regions is known to be very high, as the fraction of the TiO$_2$ powders to the zeolite powders increased, the incident light could not be irradiated onto the backside of the TiO$_2$ particles. These results clearly indicate that an important role of the siliceous MOR zeolite or SiO$_2$ powders is the efficient irradiation of incident UV light onto all of the TiO$_2$ nano-particles without any loss of light intensity.

As reported in a previous paper, the oxidation of gaseous acetaldehyde on TiO$_2$ photocatalysts hardly proceeded in the absence of a H$_2$O vapor, however, the photocatalytic reaction was

(A) TiO$_2$

UV light

(B) TiO$_2$/Zeolite

UV light

TiO$_2$ nano-particle

zeolite

Scheme 1.

dramatically enhanced by adding small amounts of H$_2$O vapor [19]. Thus, the photocatalytic oxidation reactions of gaseous acetaldehyde with O$_2$ under UV light irradiation ($\lambda > 270$ nm) over the TiO$_2$ nano-particles blended with the hydrophobic MOR zeolite (SiO$_2$/Al$_2$O$_3$ = 240) were evaluated in the presence of a H$_2$O vapor. At first, the effect of the mechanical mixing times of these two different powder samples on the photocatalytic reactivity of TiO$_2$/MOR (A) was evaluated from the viewpoint of the dispersion of the TiO$_2$ nano-particles within the zeolite powders. When the TiO$_2$ nano-particles and zeolite powders were mechanically blended in an
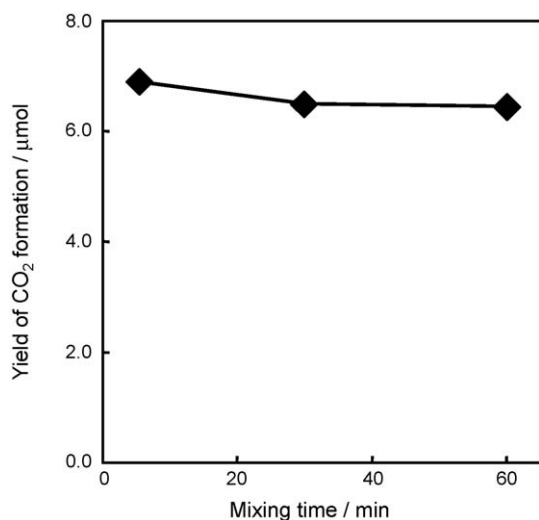

Fig. 3. Effects of the mixing time of the TiO$_2$ and zeolite powders (TiO$_2$/MOR ratio = 10/90) in an agate mortar on the photocatalytic reactivity for the oxidation of gaseous acetaldehyde with O$_2$ under UV light irradiation.
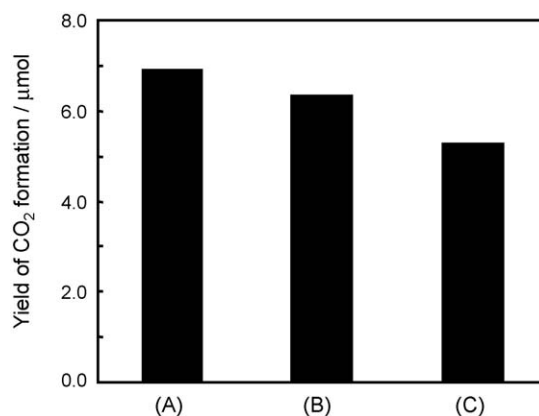

Fig. 4. Photocatalytic reactivity (UV light irradiation: 1 h) of the blended TiO$_2$/MOR samples (TiO$_2$/MOR ratio = 10/90) prepared by (A) mechanical blending, (B) an ultrasonically aqueous suspension, and (C) without mixing.

agate mortar for 60 min, the increased dispersion of TiO$_2$ nano-particles as well as the structural refinement of the micron sized zeolite crystals into submicron size could be confirmed by SEM observations (not shown). However, as shown in Fig. 3, the photocatalytic reactivity could hardly be enhanced. From this result, the mechanical mixing time of these two powders to maximize the photocatalytic reactivity of a commercial TiO$_2$ nano-particle could be optimized to be only for 5 min. For comparison, the mixed TiO$_2$/MOR (B) powders were prepared from an ultrasonically aqueous suspension. However, as shown in Fig. 4, the photocatalytic reactivity of TiO$_2$/MOR (B) was almost equivalent to TiO$_2$/MOR (A) prepared by a simple mechanical blending method. Moreover, it is notable that the TiO$_2$ and zeolite powders without mixing in an agate mortar showed slightly less photocatalytic reactivity as compared to the mechanically blended TiO$_2$/MOR (A). These results clearly indicate that the photocatalytic reactivity of the TiO$_2$ nano-particles is easily improved by simple mechanical blending with a hydrophobic zeolite powder as an adsorbent material at a low cost as well as the dispersion of the TiO$_2$ nano-particles onto the zeolite adsorbents is not an important factor for the enhanced photocatalytic oxidation of VOCs in gas phase. Especially, this simple mechanical blending method was effective for the photocatalytic oxidation of VOCs with high vapor pressures but not for the photocatalytic degradation of chemicals in aqueous solution.

Fig. 5 shows the effects of the TiO$_2$ content on the photocatalytic reactivity of the mechanically blended TiO$_2$/MOR (A) for the complete oxidation of gaseous acetaldehyde with O$_2$ in the presence of H$_2$O vapor under UV light ($\lambda > 270$ nm) irradiation. The TiO$_2$ nano-particles of ca. 5–15 wt% mechanically blended with the siliceous MOR zeolite of hydrophobic character showed almost twice as high photocatalytic reactivity as compared to the pure untreated TiO$_2$ nano-particles. Also as reported in a previous work, the siliceous zeolite can work as a good adsorbent to concentrate the gaseous acetaldehyde in hydrophobic cavities [19]. Since the siliceous zeolite does not have Brönsted acid sites, which work as strong adsorption sites for polar molecules such as H$_2$O molecules [20], the acetaldehyde molecules concentrated within the zeolite cavities could smoothly diffuse on the catalyst surfaces. In addition, as mentioned from the results of UV–vis absorption measurements, the incident UV light was efficiently irradiated on the whole part of the TiO$_2$ photocatalysts of ca. 5–15 wt% blended with the MOR zeolite due to the high transparency of the zeolite powders in UV–vis light regions. In order to verify the role of the zeolite powders, the photocatalytic reactivity of the TiO$_2$ nano-particles mechanically blended with non-porous silica
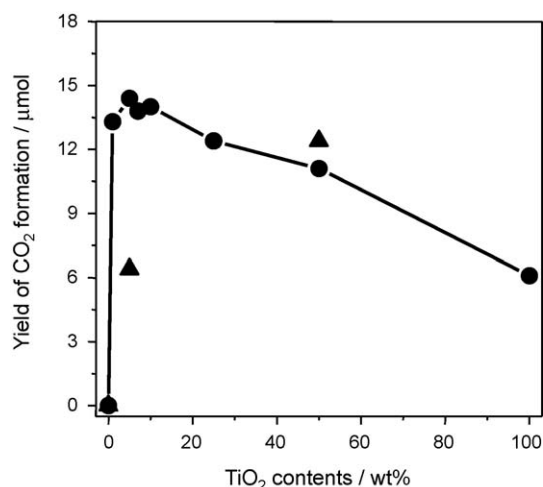
Fig. 5. Photocatalytic reactivity (UV light irradiation: 3 h) of the TiO_2 nano-particles mechanically blended with MOR (circle plots) and the non-porous SiO_2 (triangle plots) powder samples.

powders were also investigated. Although the non-porous silica (SSA_{BET} = less than $10 \, m^2/g$) adsorbed only small amounts of gaseous acetaldehyde molecules as compared to the MOR zeolite, transparent silica powders can work as an efficient diluting material for the TiO_2 nano-particles. In this case, the non-porous silica powders did not show the condensation effect for acetaldehyde molecules. Small amounts of the TiO_2 nano-particles blended with the non-porous silica powders, hence, showed low photocatalytic reactivity. From these results, the critical role of the hydrophobic MOR zeolite to enhance the photocatalytic reactivity of TiO_2 nano-particles can be concluded to be: (i) the condensation effect for gaseous acetaldehyde molecules nearby the TiO_2 photocatalytic sites; and (ii) the appropriate diluent effect of the TiO_2 photocatalysts as an intense absorber of UV light with highly transparent zeolite powders.

In order to clarify an effective use of the high-silica zeolite adsorbent for the photocatalytic oxidation of acetaldehyde in gas phase, the adsorption behaviors of acetaldehyde on the TiO_2 nano-particles and MOR zeolite powders of 30 mg were measured. As shown in Fig. 6, it was found that the TiO_2 nano-particles having
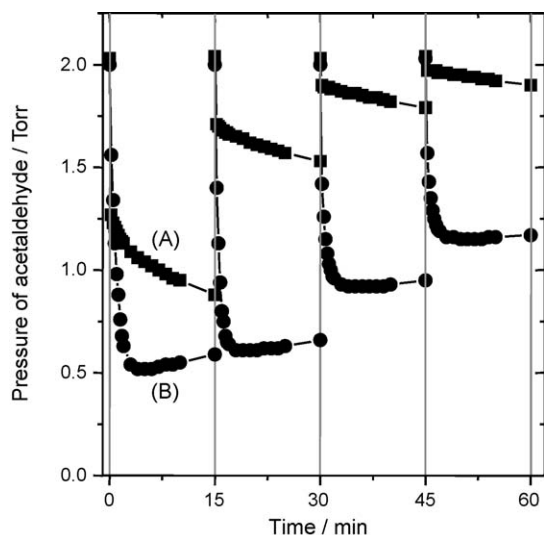

Fig. 6. Time courses in the adsorption of acetaldehyde on (A) TiO_2 nano-particles (SSA_{BET} = ca. $270 \, m^2/g$) and (B) MOR zeolite (SSA_{BET} = ca. $460 \, m^2/g$, SiO_2/Al_2O_3 = 240). Both measurements were carried out for powder samples of 30 mg.
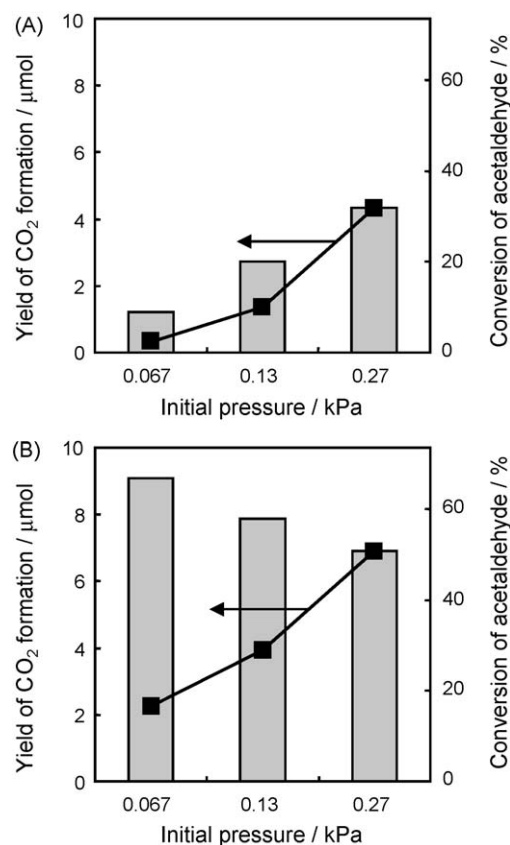

Fig. 7. Effect of the different initial pressures of acetaldehyde on the photocatalytic reactivity of: (A) TiO_2 nano-particles and (B) TiO_2 nano-particles mechanically blended with the MOR zeolite powders (TiO_2/MOR ratio = 5/95).

large surface area of ca. $270 \, m^2/g$ adsorbed large amount of acetaldehyde molecules only in early stage but immediately reached the adsorption saturation for acetaldehyde in gas phase. On the other hand, the high-silica MOR zeolite could continuously adsorb acetaldehyde molecules for a long time because the hydrophobic cavities can effectively condense the chemicals.

For further verification of the condensation of gaseous acetaldehyde molecules, the photocatalytic oxidation reaction of different initial concentrations of acetaldehyde over the TiO_2 nano-particles and TiO_2/MOR (A) were compared. As shown in Fig. 7, when only TiO_2 nano-particles were applied for the photocatalytic oxidation of gaseous acetaldehyde, the total conversion of acetaldehyde into CO_2 and H_2O was found to decrease with a decrease in the initial pressure of acetaldehyde. This result suggests that the commercial TiO_2 nano-powder without spatially ordered porous structure has large surface area of ca. $270 \, m^2/g$ but cannot effectively condense acetaldehyde molecules thinly diffused in gas phase. On the other hand, TiO_2 nano-particles mechanically blended with the hydrophobic MOR zeolite powders were found to show high and efficient photocatalytic reactivity for rather lower concentrations of gaseous acetaldehyde molecules. This result clearly indicates that the acetaldehyde molecules effectively concentrated within the hydrophobic cavities of the MOR zeolites quickly diffused onto the TiO_2 nano-particles, resulting in the efficient photocatalytic oxidation of acetaldehyde into CO_2 and H_2O under UV light irradiation. Since the concentration of gaseous acetaldehyde to be removed in home environments is generally at most 50 ppm, TiO_2 nano-particles mechanically blended with MOR zeolite powders are good candidates for the continuous removal of lower and more dilute concentrations of harmful organic compounds.

4. Conclusions

The photocatalytic properties of conventional TiO_2 nano-particles (SSP-25, Sakai Chemical Industry Co., Ltd.) could be enhanced by the simple method of mechanical blending with hydrophobic MOR zeolite powders. The optimum amount of the zeolite powders as an adsorbent for the enhancement of the photocatalytic reactivity of the blended TiO_2/MOR system was estimated to be ca. 80–95 wt% since the incident UV light was effectively irradiated onto the whole part of the TiO_2 nano-particles due to the high transparency of the siliceous zeolite powders. Furthermore, the hydrophobic zeolite powders efficiently gathered the gaseous acetaldehyde molecules within their cavities and supplied them onto the TiO_2 surfaces, resulting in the enhancement of the photocatalytic reactivity.

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